

Electrochemical water splitting on Ir and Ru oxides: an insight from *operando* photoemission spectroscopy

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Abstract

This work demonstrates the potential of Near-Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) and soft X-ray spectroscopy to probe, under dynamic reaction conditions, surface composition of active materials. *Operando* photoemission studies were performed during electrochemical oxygen evolution on Sb-doped SnO₂-supported and unsupported Ir oxides and unsupported Ru oxides in order to shed light on the nature of the active sites and probe metal-support interactions.

1. Introduction

Hydrogen production through water splitting in photochemical, photoelectrochemical or electrochemical processes has recently attracted much attention as the means for solar energy conversion and storage [1-5]. After a brief overview of various approaches and corresponding materials, we will focus on the electrochemical water splitting.

Water electrolysis (electrochemical water splitting) in proton exchange membrane (PEM) cells is considered as a promising means for sustainable hydrogen production in the megawatt scale [6]. However, its efficiency is limited by the high overpotential of the oxygen evolution reaction (OER) [7,8]. This stimulates research, which targets development of better catalytic materials for electrocatalysis of the OER. However, engineering of new more active, stable and less expensive materials requires understanding the nature of the active OER sites, the reaction and eventual degradation mechanisms.

In this presentation we will focus on the OER on Ir and Ru oxides, the most active electrode materials among the few, which can withstand harsh environment of the anode of a PEM electrolyzer [7,8]. We will discuss their structure and electrochemical properties, and show how application of Near-Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) and complementary soft X-ray spectroscopy (NEXAFS) can help in the understanding of the nature of the active sites.

2. Experimental

IrO₂, RuO₂ and mixed Ir_xRu_{1-x}O₂ thermal oxides were prepared by thermal oxidation of Ir, Ru or IrRu

metal nanoparticles, correspondingly [9]. Their characterization by X-ray powder diffraction and transmission electron microscopy confirmed their crystalline (rutile) structure. Electrochemical non-stoichiometric thin layer Ir@IrO_x and Ru@RuO_x hydrous oxides were prepared by electrochemical oxidation of Ir and Ru nanoparticles [10,11]. Sb-doped SnO₂ supported IrO_x samples were prepared as described in Ref. [12] NAP-XPS measurements were performed using membrane-electrode assemblies with Ru- and Ir- based anodes as the working electrodes and commercial Pt/C as the counter electrode. These were integrated in the electrochemical cell combined with the NAP-XPS spectrometer as described in Ref. [9].

3. Results and Discussion

Operando NAP-XPS measurements performed during the electrochemical OER evidenced significant differences in the surface state of Ir- and Ru-based anodes. Ru oxide catalyzes the OER via the so-called cation red-ox mechanism, whereby Ru(IV) is oxidized to higher oxidation states (Ru(VI) and Ru(VIII)), further evolving O₂. Closing the catalytic cycle results in an irreversible transformation of rutile structure into amorphous Ru(IV) hydroxide, resulting in material's degradation [9].

Contrariwise, Ir-based anodes operate via an anion red-ox mechanism whereby oxygen anions are oxidized to form a reactive electron deficient O⁻ species, which further react to form O₂ molecules [13,14]. Ir cations undergo the Ir(III)/Ir(IV) transition, but this occurs below the oxygen evolution onset, while during the OER they preserve their Ir(IV) oxidation state (Fig.1), no higher oxidation states (Ir(V) or higher) being observed. This mechanism was

discovered using complementary NAP-XPS and NEXAFS spectroscopy at the O K edge [11, 13]. Furthermore, we confirmed universality of the anion red-ox mechanism, which is characteristic of electrocatalysis on the Ir anodes regardless their nature: thermal crystalline IrO₂ or electrochemical non-stoichiometric Ir@IrO_x [13].

Then, we studied Ir nanoparticles, which were supported on Sb-doped SnO₂ oxide and electrochemically oxidized to produce a thin layer of IrO_x oxide on their surfaces. Sb doping ensures electronic conductivity of the support material, while the small size of Ir nanoparticles (2 nm) and strong Ir metal – SnO₂ support interactions result in the catalytic activity enhancement [12], thus allowing one to greatly decrease the amount of scarce and expensive Ir at the anode. By applying NAP-XPS under dynamic operation conditions of a water electrolyzer, we study the metal-support interactions and propose the origin of the catalytic activity enhancement of Ir@IrO_x/SnO₂-Sb vs. Ir@IrO_x [15].

4. Conclusion

This work shows the potential of NAP-XPS and soft X-ray spectroscopy to probe, under dynamic reaction conditions, surface composition of electrocatalytic materials, unveil the nature of the active sites and propose the mechanism of their degradation. It allowed us to propose different oxygen evolution mechanisms on Ru and Ir oxides and probe metal-support interactions in Sb-SnO₂-supported Ir@IrO_x nanoparticles.

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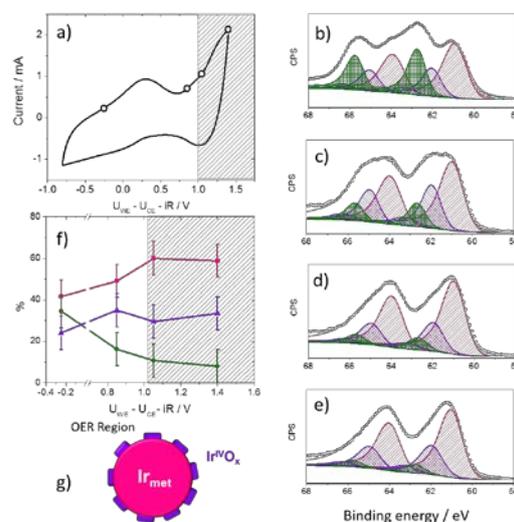


Fig.1: a) Cyclic voltammogram plotted vs. Ohmic drop corrected voltage between the working Ir@IrO_x electrode and the counter Pt/C electrode (U_{WE-CE}). b)-e): Ir4f XPS spectra at different U_{WE-CE} : -0.25V (b); 0.85V (c); 1.05V (d); 1.4V (e). c) Potential dependence of the Ir components. The OER region is marked according to the MS data. d) Scheme illustrating the structure of Ir/IrO_x nanoparticles under the OER conditions. Color codes: Ir met (pink); Ir III (olive); Ir IV (violet), fitted line (grey). The raw data are presented as open circles. Measurements are performed at RT under 3 mbar water vapor and photon energy 595 eV (From Ref. [11]).